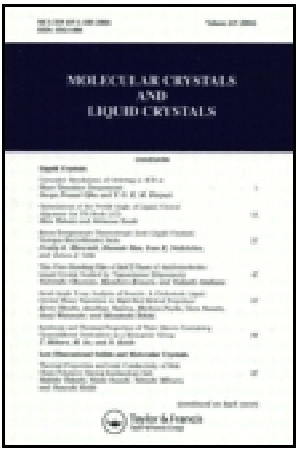


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Chromic Phase Transition in Hydrogen Bonded Polydiacetylenes

V. Shivshankar [a], Changmo Sung [b], Sukant K. Tripathy [a], Jayant Kumar [c] & Daniel J. Sandman [a]

[a] Center for Advanced Materials, Departments of Chemistry, Massachusetts, 01854-2881, USA

[b] Chemical and Nuclear Engineering, Massachusetts, 01854-2881, USA

[c] Physics and Applied Physics University of Massachusetts Lowell, Lowell, Massachusetts, 01854-2881, USA

To cite this article: V. Shivshankar, Changmo Sung, Sukant K. Tripathy, Jayant Kumar & Daniel J. Sandman (1996): The Chromic Phase Transition in Hydrogen Bonded Polydiacetylenes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 277:1, 323-330

To link to this article: http://dx.doi.org/10.1080/10587259608046037

Mol. Cryst. Liq. Cryst., 1996, Vol. 277, pp. 323–330
Reprints available directly from the publisher
Photocopying permitted by license only

THE CHROMIC PHASE TRANSITION IN HYDROGEN BONDED POLYDIACETYLENES

V. SHIVSHANKAR*, CHANGMO SUNG**, SUKANT K. TRIPATHY*,
JAYANT KUMAR#, AND DANIEL J. SANDMAN*
Center for Advanced Materials, Departments of Chemistry*, Chemical and Nuclear
Engineering**, and Physics and Applied Physics# University of Massachusetts
Lowell, Lowell, Massachusetts 01854-2881 USA

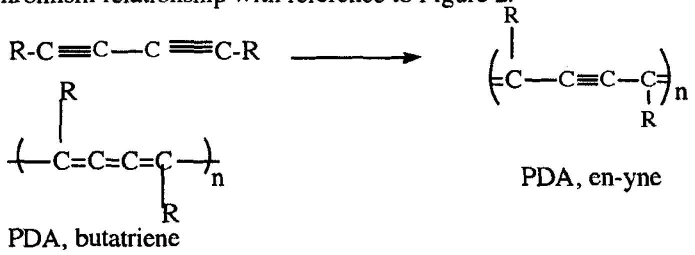
Abstract Thermochromism in the polydiacetylenes(PDA) from the alkylurethanes of 5,7-dodecadiyn-1,12-diol is associated with a first order phase transition involving the expansion of the crystallographic unit cell, the preservation of the urethane hydrogen bonding, and possibly some relief of mechanical strain upon heating. Insights into thermochromism obtained from recent studies of nonthermochromic forms of PDA-ETCD are presented. Initial observations of the surfaces of single crystals of several PDA in this class by atomic force microscopy are consistent with known crystallographic data.

INTRODUCTION

As a class, the polydiacetylenes(PDAs) provide several examples of the best defined polymers in that they are rigorously defined in terms of composition and chain sequence. As a result of their synthesis by topochemical and topotactic solid state polymerization, many PDAs are available in the form of macroscopic single crystals, thin film single crystals, Langmuir-Blodgett films, and other very highly ordered forms. Hence, their properties can be more unambiguously interpreted than those of other classes of polymers.[1]

In this work, we are concerned with a specific subclass of PDAs, namely the alkyl urethanes of 5,7-dodecadiyne-1,12-diol(1). The molecular and repeat structures of these materials are given in Figure 1. These hydrogen-bonded PDAs have received considerable attention following initial reports of thermochromism in the ethyl[2](ETCD, 1a) and isopropyl[3](IPUDO, 1b) derivatives. Thermochromism in these conjugated polymers is manifested by a shift of the maximum of the electronic spectrum from about 630-640 nm to about 540 nm. The changes in crystal structure that occur in the course of the thermochromic phase transition, and the crystal structure-linear spectroscopy relationship are topics of central interest in the study of these materials.

The crystal structures of the materials under discussion are known from the similarity of their lattice constants to those of PDA-TCDU(1d), an example where the complete structure has been determined.[4] The lattice constants of these polymers involve a 4.9 Å chain repeat distance, a constant related to inter-layer distance, and a constant related to the length of the side groups.[5] A representation of a relevant portion of the crystal structure is given in Figure 2. It is convenient to discuss the crystal structure-thermochromism relationship with reference to Figure 2.



R = -$(CH_2)_4$-O-C(O)-NH-R', 1

R' = -C_2H_5, ETCD, 1a
R' = *i*-C_3H_7, IPUDO, 1b
R' = *n*-C_3H_7, PUDO, 1c
R' = C_6H_5, TCDU, 1d

Figure 1. Diacetylene polymerization and molecular structures of the urethane derivatives under discussion.

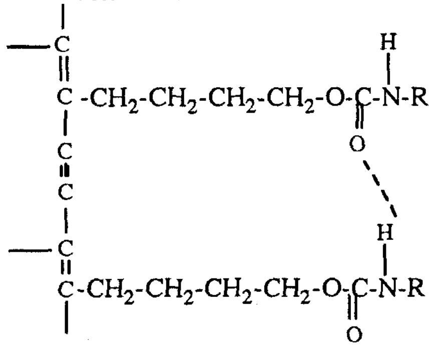


Figure 2. Schematic representation of a portion of the structure of a PDA such as -ETCD or -IPUDO.

FTIR[6] and solid state NMR[7] spectroscopies established that the hydrogen-bonding of the urethane group was preserved in the course of the thermochromic transition. The NMR spectra[7] ruled out the possibility of the involvement of the butatriene form(Figure 1) of the backbone, as the acetylenic ^{13}C resonance was observed below and above the temperature of the transition. X-ray powder diffraction studies[5,8-10] indicated that the crystallographic unit cell volume increases above the temperature of the phase transition which is clearly first order. The major changes in the crystal structures involve the lattice constants other than that associated with the backbone repeat. Calorimetric studies[10] ruled out the possibility that monomer melting plays a significant role in the thermochromic phase transition of PDA-IPUDO, 1b.

The wavelengths of maximum absorption at room temperature of 1a and 1b are comparable to those of PDA crystals that have polarizable π-electron systems closer to the backbone. It is widely held[11-13] that side group polarizability is an important factor in determining the wavelength of PDA maximum absorption. The similarity in excitation energy for the alkyl urethane PDA, 1, with 4 CH_2 groups between the backbone and the urethane group, and PDA with polarizable π-electron systems one CH_2 group from the backbone, merits further investigation.

It is useful to discuss the spectral changes associated with PDA thermochromism in the same framework used for organic solids and PDA.[11-13] The observed solid state transition energy, E_k, is typically discussed in terms of E_o, the transition energy for an isolated gas phase species, D, which summarizes the energetics of the gas-to-crystal shift, and $I(k)$, a term that deals with the exciton transfer interaction between translationally equivalent and nonequivalent moieties in the solid state(Equation 1). It is of interest to

$$E_k = E_o + D + I(k) \tag{1}$$

assess the magnitude of potential changes in E_o and D in the course of the thermochromic phase transition.[14] An attempt to discuss the various contributions to the terms in Equation 1 with reference to urethane-substituted PDA was recently reported.[15]

In this paper, we discuss a new synthesis of PDA-PUDO(1c), recent results concerning the nonthermochromic forms of PDA-ETCD, and some initial observations of the surfaces of single crystals of PDA-ETCD and -IPUDO by atomic force microscopy.

SYNTHESIS OF PDA-PUDO

PDA-PUDO has been of particular interest in connection with its thermochromism[16] and a report of photochromic behavior.[17] To avoid problems associated with impurities,[18] we choose to synthesize the monomeric alkyl urethanes by Hay coupling of the urethane-substituted monoacetylenes. The specific reactions for PUDO are given in Figure 3.

A methanol solution of the monoacetylene[18](3.66g., 0.02 mole) was added to a flask containing methanol(25ml.), tetramethylethylenediamine(TMEDA, 0.3g., 0.26 mmole) and cuprous chloride (0.4g, 0.4 mmole) over a period of 1 hour with constant magnetic stirring. Oxygen was bubbled through the reaction mixture, and the solution turned blue and muddy. The reaction was monitored by IR spectrum until the peak at 2120 cm^{-1} disappeared. Hydrochloric acid(5N, 20 ml) was added to the mixture which turned green. The solid product was filtered, recrystallized from ethyl acetate, and vacuum dried. Extremely light sensitive white crystals were obtained in 90% yield, m.p. 123°.

PUDO monomer was polymerized with ^{60}Co γ-radiation using a dose of 60 Mrad over a period of 60 hours. The conversion of monomer to polymer was 95%, as judged by extraction with methanol. The X-ray powder diffraction pattern was consistent with the previously reported[16] lattice constants for PDA-PUDO.

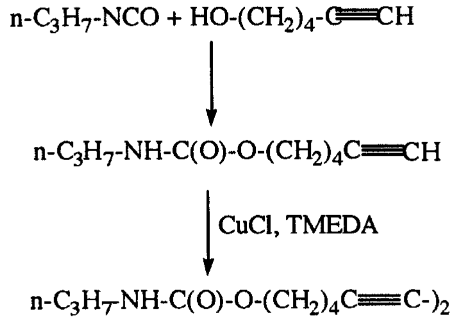


Figure 3. Synthetic route to PUDO(<u>1c</u>) monomer.

NONTHERMOCHROMIC FORMS OF PDA-ETCD

When single crystals of PDA-ETCD are exposed to boiling chlorobenzene(b.p. 130°C), the crystals turn red because they are above the temperature of the phase transition, and the solution is colored orange as a result of extraction of 15-20 % of the original weight[14,19,20] as monomer and oligomer. When the crystals return to room temperature, they remain red, largely retain their original shape, and no longer exhibit thermochromism. While extraction of monomer from other partially polymerized alkyl-urethane substituted PDA results in a spectral shift to higher energy,[21] monomer extraction of PDA-ETCD with methanol or ethyl acetate does not result in a spectral shift[2b].

X-ray powder diffraction studies of crystals exposed to the boiling solvent for 48 hours indicate that the diffusion of solvent into the crystal has expanded the lattice. The *h00* reflections indicate a single phase and are broader than those of the pristine polymer suggesting either smaller crystallite size or increased disorder. The density of the crystals extracted with boiling chlorobenzene for 48 hours approaches the density calculated[5] for the high temperature red form of PDA-ETCD. The anisotropic reflection spectra of these red crystals exposed to boiling solvent for either 2-3 minutes or 48 hours reveal a shift of 3500 cm^{-1} to higher energy of the most intense spectral transition relative to pristine PDA-ETCD. These spectra also show structure on the low energy side of the most intense absorption peaks, and this structure was attributed[20] to residual thermochromic PDA-ETCD in the modified crystals, presumably near the crystal surface.

Additional information concerning phase homeogeneity may be obtained from Raman spectroscopy, which is primarily a probe of surface regions of crystals. Using

Fourier-transform(FT) Raman spectroscopy with excitation at 1064 nm[22], pristine PDA crystals exhibit Raman shifts of 2078 and 1452 cm^{-1} for the normal modes associated with triple bond and double bond stretching, respectively, at room temperature. These data are in good agreement with previous studies using 632.8 nm as wavelength of excitation.[23] The FT-Raman spectrum of PDA-ETCD exposed to boiling chlorobenzene for 48 hours is shown in Figure 4. While the region of triple bond stretching exhibits one shifted line at 2119 cm^{-1}, the region of double bond stretching contains two shifted lines, a strong line at 1524 cm^{-1} and a weaker line at 1488 cm^{-1}. The presence of two shifted lines in the double bond stretching region is taken as an indication that there is more than one environment for double bonds in the material. The Raman spectrum is consistent with the previous suggestion[20] that there is more than one phase in the nonthermochromic form of PDA-ETCD.

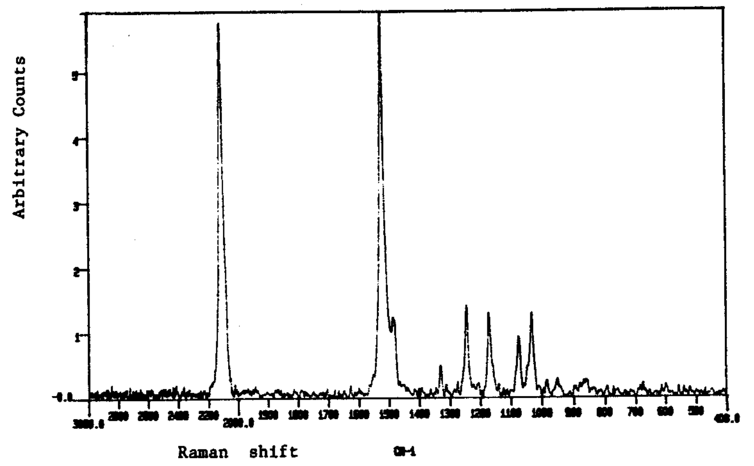


Figure 4. FT-Raman spectrum of nonthermochromic PDA-ETCD.

The interaction of hot chlorobenzene with PDA-ETCD causes expansion of the lattice, some disordering of the polymer chains, and the removal of interactions that permit observation of thermochromism. At present, we find it an attractive hypothesis to assume that room temperature electronic spectra of PDA-ETCD reflect compressive mechanical strains on the backbone that are partially relieved as the material is heated. Chain direction lattice constants significantly less than 4.90-4.91Å reported[19,24] may be taken as evidence for such a compression. Hence, the thermochromic phase transition involves changes in both E_0 and D in Equation 1.

ATOMIC FORCE MICROSCOPY(AFM) OF POLYDIACETYLENE CRYSTALS

We were motivated to study surface morphology of PDA crystals by AFM as a result of studies of Raman spectra of various PDA in which dispersion of the Raman spectrum was observed.[25,26] From these studies, it was concluded that pristine PDA crystals have disordered surface phases. Concurrently with these studies[25,26] was the first report of an AFM study of a PDA crystal. This study concluded that the substituent positions of a PDA crystal surface layer were different from those of the bulk.[27] Additionally, indications that the surface structure of PDA-IPUDO varies from crystal-to crystal were found in Raman studies using 514.5 nm excitation at room temperature.[28]

Previously, Yamada, et al., investigated cleaved surfaces of two PDA single crystals and have reported that the periodicity in the observed images is consistent with the unit cell of the bulk crystal structure.[29]

We have investigated the free standing single crystals of the monomeric and polymeric forms of ETCD and IPUDO by Atomic Force Microscopy (AFM). Micron (10-100μ) scale as well as molecular resolved images were obtained.

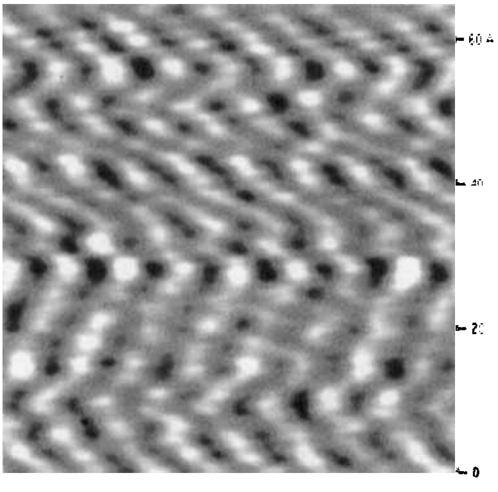


Figure 5. AFM image of a PDA-ETCD single crystal; the *b* -axis is vertical. See Color Plate IV.

AFM imaging was carried out with a Scanning Probe Microscope "Autoprobe CP" (Park Scientific Instruments) under ambient conditions. The constant force (topographic) imaging mode was used for large scale scans and constant height (error) mode was used for obtaining molecular images. Si_3N_4 cantilevers (Park Scientific Instruments,) with a force constant of 0.06 N/m were used. The molecular scale images were processed using the 2-D Fast Fourier Transform (FFT) technique available in the Autoprobe Image Processing software. The large scale scans show a fibrillar structure of the polymeric crystal while the molecular images reveal a backbone repeat of about 5Å and a side chain related distance[15] of about 7Å. Figure 5 reveals a molecular image of PDA-ETCD indicating a relatively disordered surface. The images of PDA-IPUDO are quite similar to those of PDA-ETCD. This is expected due to their similar structures, morphology, and packing arrangement.[10] These numbers also correspond to the crystallographic data obtained from X-ray diffraction techniques.

ACKNOWLEDGEMENTS

This work was supported in part by the U.S. Air Force Office of Scientific Research under Grant F49620-95-1-0179 and the Office of Naval Research. Access to the University of Massachusetts Lowell ^{60}Co source was facilitated by Ms. M. Montesalvo.

REFERENCES

1. D.J. Sandman, Trends Polym. Sci., 2, 44(1994).
2. (a) G.J. Exarhos, W.M. Risen, Jr., and R.H. Baughman, J. Am. Chem. Soc., 98, 481 (1976); (b) R.R. Chance, R.H. Baughman, H. Müller, and C.J. Eckhardt, J. Chem. Phys., 67, 3616(1977).
3. H. Eckhardt, C.J. Eckhardt, and K.C. Yee, J. Chem. Phys., 70, 5498(1979).
4. (a) V. Enkelmann and J.B. Lando, Acta Cryst., B34, 2352(1978);(b) A. Kobayashi, H. Kobayashi, Y. Tokura, T. Kanetake, and T. Koda, J. Chem. Phys., 87, 4962 (1987).
5. M.J. Downey, G.P. Hamill, M. Rubner, D.J. Sandman, and C.S. Velazquez, Makromol. Chem., 189, 1199(1988).
6. M.F. Rubner, D.J. Sandman, and C.S. Velazquez, Macromolecules, 20, 1296(1987).
7. H. Tanaka, M.A. Gomez, A.E. Tonelli, and M. Thakur, Macromolecules, 22, 1208 (1989).
8. H. Tanaka, M.A. Gomez, A.E. Tonelli, A.J. Lovinger, D.D. Davis, and M.K. Thakur, Macromolecules, 22, 2427(1989).
9. S. Koshihara, Y. Tokura, K. Takeda, T. Koda, and A. Kobayashi, J. Chem. Phys., 92, 7581(1990).
10. S.H.W. Hankin, M.J. Downey, and D.J. Sandman, Polymer, 33, 5098(1992).
11. M. Schott and G. Wegner, in Nonlinear Optical Properties of Organic Molecules and Crystals, edited by D.S. Chemla and J. Zyss(Academic Press, Orlando, FL, 1987), Vol. 2, pp. 3-49.
12. R.J. Hood, H. Müller, C.J. Eckhardt, R.R. Chance, and K.C. Yee, Chem. Phys. Lett., 54, 295(1978).

13. D.N. Batchelder, in Polydiacetylenes, edited by D. Bloor and R.R. Chance(Martinus Nijhoff, Dordrecht, Boston, 1985), pp. 187-212.
14. D.J. Sandman, M.J. Downey, and S.H.W. Hankin, in Electrical, Optical, and Magnetic Properties of Organic Solid State Materials, edited by A.F. Garito, A.K-Y. Jen, C.Y-C. Lee, and L.R. Dalton, Materials Research Society Symposium Proceedings Volume 328, 1994, pp. 101-106.
15. A.J. Campbell and C.K.L. Davies, Polymer, 36, 675(1995).
16. S. Koshihara, Y. Tokura, K. Takeda, T. Koda, and A. Kobayashi, J. Chem. Phys., 92, 7581(1990).
17. S. Koshihara, Y. Tokura, K. Takeda, and T. Koda, Phys. Rev. Lett., 68, 1148 (1992).
18. D.J. Sandman, L.A. Samuelson, and C.S. Velazquez, Polymer Commun., 27, 242 (1986).
19. D.J. Sandman, M.J. Downey, and S.H.W. Hankin, Makromol. Chem., 194, 3433 (1993).
20. C.A. Sandstedt, C.J. Eckhardt, M.J. Downey, and D.J. Sandman, Chem. Mater., 6, 1346(1994).
21. G.N. Patel and G.G. Miller, J. Macromol. Sci.-Phys., B20, 111(1981).
22. D.J. Sandman, L. Li, S. Tripathy, J.C. Stark, L.A. Acampora, and B.M. Foxman, Organometallics, 13, 348(1994).
23. D.J. Sandman and Y.J. Chen, Synthetic Metals, 28, D613(1989).
24. C. Brouty, P. Spinat, and A. Whuler, Acta Cryst., C44, 1070(1988).
25. S.H. Hankin and D.J. Sandman, Macromolecules, 24, 4983(1991).
26. S.H.W. Hankin and D.J. Sandman, in Structure-Property Relations in Polymers, edited by M.W. Urban and C.D. Craver(American Chemical Society Advances in Chemistry Series, Volume 236, 1993), Chap. 8, pp. 243-262.
27. S.N. Magonov, G. Bar, H.-J. Cantow, H.-D. Bauer, I. Müller, and M. Schwoerer, Polymer Bull., 26, 223(1991).
28. S.H.W. Hankin and D.J. Sandman, in Electrical, Optical, and Magnetic Properties of Organic Solid State Materials, edited by L.Y. Chiang, A.F. Garito, and D.J. Sandman, (Materials Research Society Symposium Proceedings Volume 247, 1992), pp.661-667.
29. H. Yamada, S. Okada, T. Fujii, M. Kageshima, A. Kawazu, H. Matsuda, H. Nakanishi, and K. Nakayama, Applied Surface Science, 65/66, 366-370 (1993).